Changes in the Forms of Cadmium with Time in Some Western Australian Soils

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Abstract

Changes in the forms of Cd with time could affect its uptake by plants and hence potential toxicity to animals and humans. The effect of time on the forms of native and added Cd was studied in four West Australian soils which differed in their clay, hydrous oxide and organic matter content. Sequential extraction of soluble (KCl), exchangeable ($BaCl_2$), bound to organic matter (NaOCl), bound to oxides/clays (ammonium oxalate) and residual (concentrated acids) forms of Cd was carried out at different time intervals after the addition of Cd.

The Cd that was added to the soils transformed with time to less soluble forms; the extent depending upon the type of soil. In addition, the rate of transformation in a particular type of soil was affected by both pH and rate of Cd addition. Soluble cadmium in the sandy soil decreased with time whereas the exchangeable form increased. The extent of the changes increased with increase in pH. In the peaty sand at pH $\leq$5, exchangeable Cd increased apparently at the expense of soluble Cd. At higher pH values, however, Cd bound to organic matter increased with time as exchangeable Cd decreased. In the lateritic podzolic soil (dominated by kaolinite), there was no effect of time on the forms of Cd at pH values $\leq$5. At pH $\geq$6, the exchangeable form of Cd decreased whereas Cd bound to organic matter and residual Cd increased with time. In the yellow earth (dominated mainly by goethite), soluble Cd decreased with time at pH values $\leq$5 and became a negligible fraction at pH 6. Exchangeable Cd decreased with time at pH values $\geq$5 whereas Cd bound to oxides and residual Cd increased with time at all the pH values.

Introduction

Cadmium (Cd) has accumulated in some Australian soils due to the application of phosphatic fertilizers to overcome phosphorus deficiencies in crops (Williams and David 1973). The extent of the build up of Cd varies with the type of soil, Cd content in the fertilizers and the management practices involved (Mortvedt *et al.* 1981; Tiller *et al.* 1984; Rothbaum *et al.* 1986; Barrow 1987; Alloway 1990; Mann and Ritchie 1993). Cadmium has been shown to adsorb onto soil surfaces very quickly with virtually no changes observed with time (Sidle and Kardos 1977; King 1988). In other studies, however, adsorption continued for longer periods of time (Brummer *et al.* 1988). The retention of Cd or any other metal by soils appears to be a multistep process involving an initial fast adsorption (from soil solution to external soil surface) followed by slow adsorption, i.e. diffusion

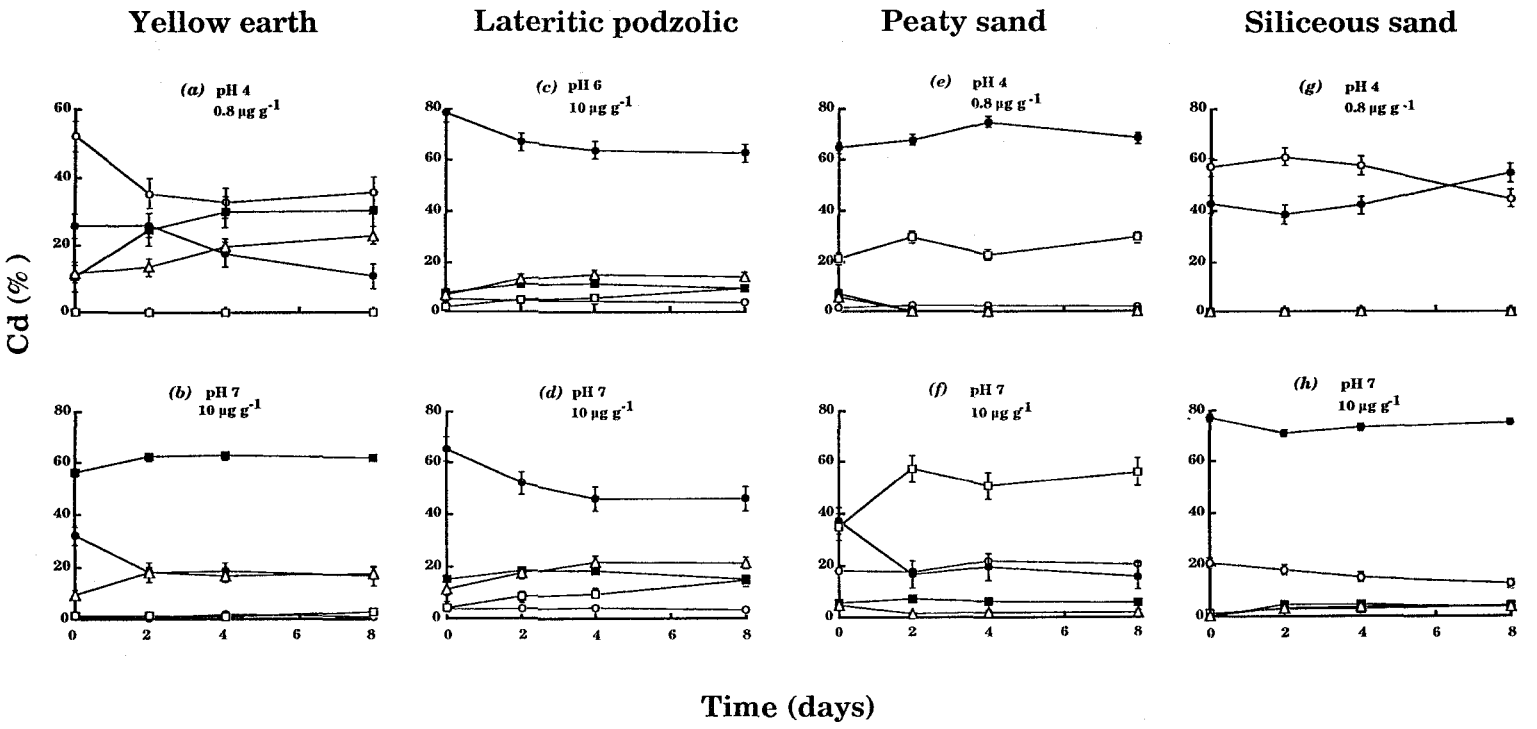

Fig. 1. Relationship between time and forms of Cd [% soluble Cd (○), % exchangeable Cd (●), % Cd bound to organic matter (□), % Cd bound to oxides/clays (■) and % residual Cd (▲)] in the yellow earth (*a*) at pH 4 and at 0·8 μg Cd g^{-1}, (*b*) at pH 7 and at 10 μg Cd g^{-1}; in the lateritic podzolic (*c*) at pH 6 and at 10 μg Cd g^{-1}, (*d*) at pH 7 and at 10 μg Cd g^{-1}; in the peaty sand (*e*) at pH 4 and at 0·8 μg Cd g^{-1}, (*f*) at pH 7 and at 10 μg Cd g^{-1}; in the siliceous sand (*g*) at pH 4 and at 0·8 μg Cd g^{-1}, (*h*) at pH 7 and at 10 μg Cd g^{-1}. Vertical bars denote standard errors.

into pores of inner soil surfaces (Kinniburgh and Jackson 1981; Aringhieri *et al.* 1985; Brummer *et al.* 1988).

Most studies of the effect of time on Cd retention have not distinguished between the effect of time on Cd retention by different soil components. The changes in retention of Cd with time will depend on the type of components present in a soil and the factors that affect the retention by each component. Mann and Ritchie (1993) found that pH was a major factor that affected the extent of retention by different components which ultimately affected the proportion of the forms of Cd in each soil.

The effect of time on retention may have important implications for Cd uptake by plants and hence Cd accumulation in the food chain. If Cd moves into less available forms with time, there will be less danger of its uptake by plants (Brams and Anthony 1988; Bell *et al.* 1991). There is some evidence that Cd availability to plants decreases with time (Street *et al.* 1978).

The objective of this research was to study the effect of time on the forms of Cd extracted by a sequential extraction scheme at different pH values and at different rates of Cd addition in four soils. The soils were chosen according to their hydrous oxide, organic matter and clay contents.

Materials and Methods

Soils

The soils used in this study came from virgin sites and were a yellow earth, a lateritic podzolic, a peaty sand and a siliceous sand. They were described in detail by Mann and Ritchie (1993). Phosphorus fertilizers had not been applied to the soils previously and hence any Cd found in the unamended soils is referred to as native Cd.

Incubation Procedure

A quantity of 200 g of each soil was taken and the soil solution pH was adjusted to 4·0, 5·0, 6·0 and 7·0 as described by Mann and Ritchie (1993). Cadmium was added as a $Cd(NO_3)_2$ solution to achieve 0, 0·8, 3·2 and 10·0 μg Cd g^{-1} and then incubated at 40±1°C (Mann and Ritchie 1993) for 0, 2, 4 and 8 days. At the end of each incubation period, sufficient soil was removed from each treatment to carry out sequential extractions on three replicates. Each subsample was frozen until the extractions were carried out. A sequential extraction scheme (Mann and Ritchie 1993) was carried out on each subsample to estimate soluble Cd (extracted by 0·005 M KCl), exchangeable Cd (extracted by 0·1 M $BaCl_2$), Cd bound to organic matter (extracted by 5·3% NaOCl, pH ≈ 8·5), Cd bound to oxides/clay (extracted by ammonium oxalate solution) and residual Cd (extracted by concentrated acids).

Analysis of Cd

Cadmium in different extracts was determined by flame atomic absorption spectrophotometry (FAAS) or by using a graphite furnace (GFAAS; Mann and Ritchie 1993). The accuracy of the method was tested by Mann (1993).

Results

The effect of time on the amount and percentage of total Cd (% Cd) in each extract varied with the type of soil, pH and with rates of Cd addition. The general trends for each soil are summarized in Fig. 1. Cadmium extracted and % Cd in each fraction varied with time in a similar manner and hence the results will be reported for % Cd only.

Forms of Native Cd

In the absence of added Cd, acid-extractable Cd was the only fraction observed in the yellow earth and lateritic podzolic soil and it did not change with time at any pH. No native Cd was detectable in the peaty sand and siliceous sand.

Forms of Added Cd

Yellow earth

The % Cd-KCl decreased in the first 2 days of incubation at pH $\leq$5 for all the application rates studied (e.g. Figs 1*a* and 1*b*). The % Cd-$BaCl_2$ decreased with time at all pH values and at all rates except at pH 4 where a decrease was only noticed in the presence of 0·8 μg Cd g^{-1} (Figs 1*a* and 1*b*). At all pH values, % Cd-$BaCl_2$ tended to decrease over the complete incubation period at an application rate of 0·8 μg g^{-1} (e.g. Fig. 1*a*). At other rates, a significant decrease in % Cd-$BaCl_2$ was noticed only up to the second day of incubation (Fig. 1*b*).

The % Cd-NaOCl was <3% of total Cd and therefore considered negligible (Figs 1*a* and 1*b*). The % Cd-ammonium oxalate (% Cd-AO) increased with time at all the pH values and at all the rates of Cd application (Figs 2*a* and 2*b*). The rate of increase in % Cd-AO decreased with increasing time, pH and application rate of Cd. The maximum increase in % Cd-AO was observed within the first 2 days of incubation (Fig. 2*b*).

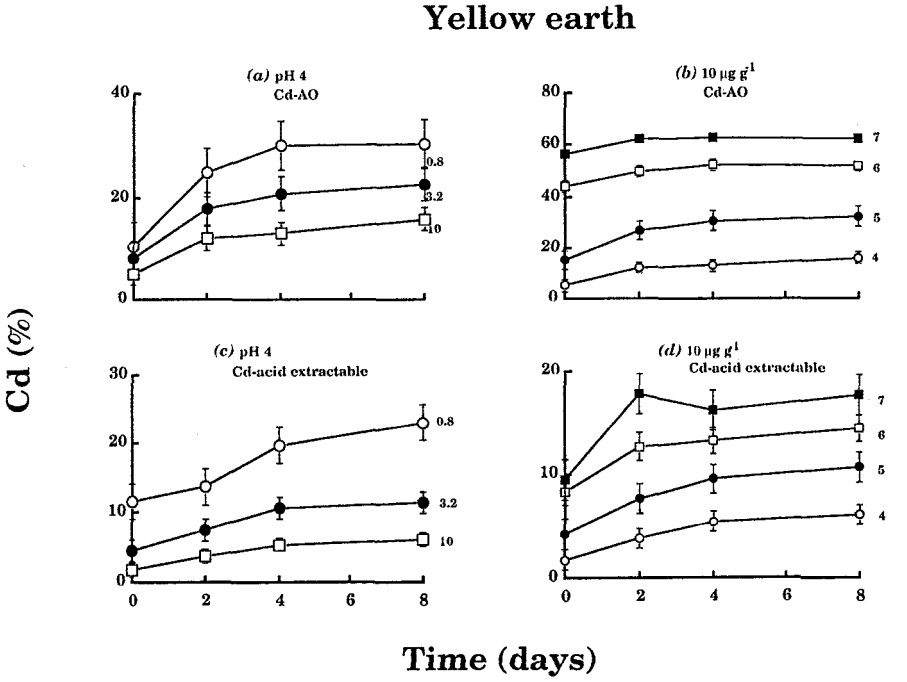

Fig. 2. Relationship between time and (*a*) % Cd bound to oxides; (*c*) % residual Cd at pH 4 and at Cd application rates 0·8 μg Cd g^{-1} (○), 3·2 μg Cd g^{-1} (●), and 10 μg Cd g^{-1} (□); and (*b*) % Cd bound to oxides; (*d*) % residual Cd at 10 μg Cd g^{-1} rate and at pH values 4 (○), 5 (●), 6 (□) and 7 (■) in the yellow earth. Vertical bars denote standard errors.

The % Cd-acid extractable tended to increase with time at all the rates and at all the pH values (Figs 2*c* and 2*d*). At pH 4, the extent of increase with time decreased with increasing application rate (Fig. 2*c*). At Cd application rates $>0{\cdot}8\ \mu g\ g^{-1}$, the rate of increase in % Cd-acid extractable decreased with time and became negligible after 2 days (Fig. 2*d*).

Lateritic podzolic

The amount of all the forms of Cd at pH 4 and 5 did not change with time at any of the rates of Cd application (data not shown). At pH 6 and 7, however, changes in concentration of all forms of Cd were observed with time except for % Cd-KCl and % Cd-AO (Figs 1*c* and 1*d*). The % Cd-$BaCl_2$ decreased curvilinearly by 15–20% after 8 days at pH $\geq$6 and at Cd rates $\geq 3{\cdot}2\ \mu g\ g^{-1}$ (e.g. Fig. 3*a*). At $0{\cdot}8\ \mu g\ g^{-1}$ Cd application, and at pH 6 and 7, % Cd-$BaCl_2$ varied inconsistently with time. The % Cd-NaOCl increased 5–10% after 8 days incubation at all the rates of Cd application at pH 6 and 7 (e.g. Fig. 3*b*). At pH 6, an increase in % Cd-acid extractable was observed up to the second day of incubation at all the rates of Cd application (Fig. 3*c*). At pH 7, a linear increase with time in % Cd from 25 to 40% was observed at $0{\cdot}8\ \mu g\ g^{-1}$ Cd rate whereas, at other rates, an increase of nearly 10% was observed up to the fourth day and thereafter remained constant (Fig. 3*d*).

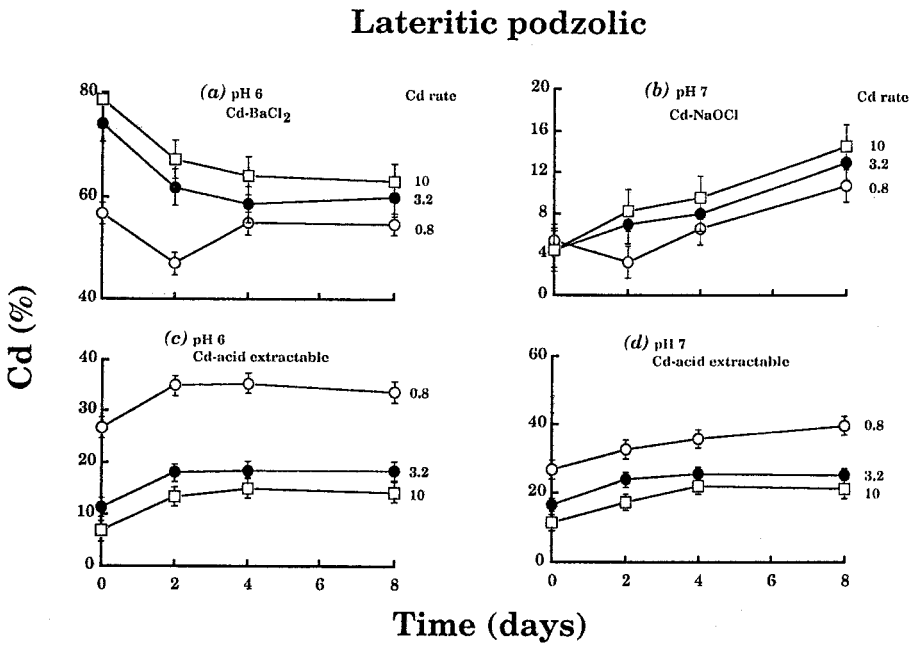

Fig. 3. Relationship between time and (*a*) % exchangeable Cd at pH 6, (*b*) % Cd bound to organic matter at pH 7, (*c*) % residual Cd at pH 6 and (*d*) % residual Cd at pH 7 at Cd application rates $0{\cdot}8\ \mu g$ Cd g^{-1} (○), $3{\cdot}2\ \mu g$ Cd g^{-1} (●) and $10\ \mu g$ Cd g^{-1} (■) in the lateritic podzolic soil. Vertical bars denote standard errors.

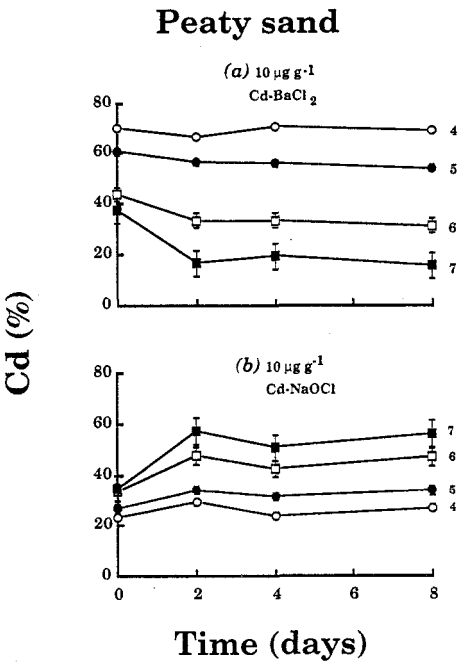

Fig. 4. Relationship between time and (*a*) % exchangeable Cd, (*b*) % Cd bound to organic matter at 10 μg Cd g^{-1} application rate and at pH values 4 (○), 5 (●), 6 (□) and 7 (■) in the peaty sand. Vertical bars denote standard errors.

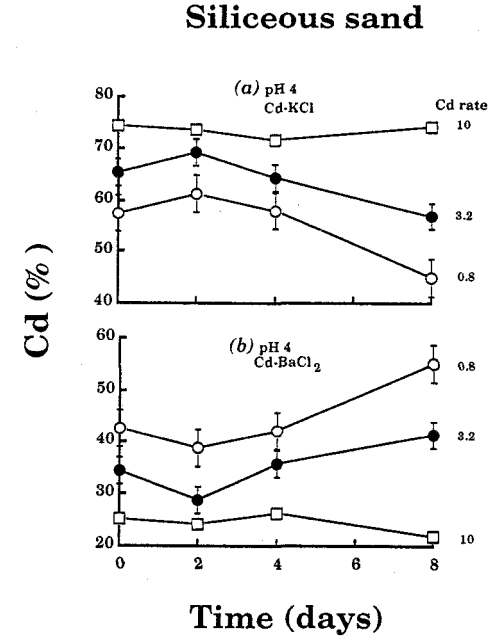

Fig. 5. Relationship between time and (*a*) % soluble Cd and (*b*) % exchangeable Cd at pH 4 and at Cd application rates of 0·8 μg Cd g^{-1} (○), 3·2 μg Cd g^{-1} (●), and 10 μg Cd g^{-1} (■) in the siliceous sand. Vertical bars denote standard errors.

Peaty sand

The % Cd-KCl tended to increase slightly (<10%) with time at all the rates of Cd application and at all the pH values except at pH 4 (Figs 1*e* and 1*f*). The % Cd-$BaCl_2$ decreased and % Cd-NaOCl increased with time up to the second

day at all the rates of Cd application at pH >5 (e.g. Figs 4*a* and 4*b*). The % Cd-AO and the % Cd-acid extractable were a small fraction (<10%) of the total Cd applied to the soil and did not change significantly with time.

Siliceous sand

The % Cd in the KCl extract decreased with time at all the pH values and at all the rates except at pH 4 and at an application rate of 10 μg Cd g^{-1} (Fig. 5*a*). At pH 4, the % Cd-KCl tended to decrease after 2 days of incubation at Cd rates $\leq 3 \cdot 2$ μg g^{-1} (Fig. 5*a*). The % Cd-$BaCl_2$ increased slightly with time at pH 4 at times >2 days and at Cd application rates $\leq 3 \cdot 2$ μg g^{-1} (Fig. 5*b*). At $10 \cdot 0$ μg g^{-1} application rate, no effect of time was observed at any pH. No change in the NaOCl, ammonium oxalate and acid-extractable Cd was observed at any pH values except at pH 7 where only a slight increase (<5%) in these forms was observed at all the rates of Cd application (Figs 1*g* and 1*h*).

Discussion

There was a general decline in the more soluble forms of Cd and an increase in the less soluble forms as time progressed in each soil except the peaty sand. The extent and rate of change with time of the amount of Cd in each form depended on the type of adsorbing surface, pH and application rate of Cd. In general, the more sites available for retention of Cd, the more quickly the rate of change of Cd in a particular form approached zero. In the yellow earth, for example, the rate of change approached zero within 2 days at pH 7. At pH 4, there would have been fewer negatively charged sites and the rate of change of Cd, in almost all the forms, continued for a longer period of time.

For a particular soil, the transformation also varied with the rate of Cd addition. In the yellow earth, for example, the transformation of Cd to the form bound by oxides and to residual forms continued for a longer period of time at lower rates of Cd application than at higher rates (Figs 2*e* and 2*g*). This could be due to the difference in the concentration gradient from the surface into an internal pore, created by different rates of Cd addition. At lower rates, the concentration gradient would be lower than that at higher rates and hence transformation of Cd from one form to another was slower.

The extent and rate of formation of one form will depend upon the rate of formation of all the other forms, as each reaction will be removing Cd from solution and hence will be affecting the solution concentration to different extents. However, in situations where there was negligible soluble Cd (e.g. in yellow earth and peaty sand at pH >5), a decrease in the amount of Cd in the exchangeable form occurred (e.g. Figs 2*d* and 6*c*) as more strongly bound Cd increased. In the lateritic podzolic soil at pH <5, most of the Cd was in an exchangeable form and the remainder was soluble. At higher pH values, a decrease in the exchangeable form of Cd and an increase in residual and that bound to organic matter was observed as time progressed, possibly due to the development of more strongly binding sites on the edges of kaolinite and on organic matter (Figs 3*a* and 3*b*).

In the yellow earth soil, the soluble and the exchangeable forms of Cd decreased with time, whereas Cd bound to oxides and residual Cd increased. Goethite was the major adsorption component in this soil. The rate of change of Cd with

time was affected by pH and the rate of Cd addition. A decrease in soluble Cd with time was observed at pH $\leq$5 only, presumably because of a limited number of adsorption sites present at lower pH values. Evidence for a limited number of sites can also be seen from the increase in % Cd in the soluble form (% Cd-KCl) as the application rate of Cd increased. At pH 6 and 7, soluble Cd was almost negligible (<2%) at all the rates of Cd addition, presumably because Cd is adsorbed at negatively charged sites which increase in number with pH and there were sufficient sites to adsorb almost all the Cd added, even at the highest rate of Cd application. Not only the soluble Cd declined with time, but even exchangeable Cd started to decline at higher pH values. Presumably, variable-charged negative sites developed at pH $\geq$5 and bound Cd by forces other than coulombic and/or became less accessible. Tiller *et al.* (1984) in their study also observed the transfer of non-specifically bound forms to specifically bound forms.

In the lateritic podzolic soil, time had no effect on the amount of Cd in any of the forms at pH $\leq$5 and the two major forms of Cd were soluble and exchangeable. The reaction of Cd with the kaolinitic clays was rapid as might be expected when exchange sites are mainly found on external surfaces. At pH 6 and 7, however, exchangeable Cd decreased with time while residual Cd tended to increase, reflecting a small increase in variable charged sites on the edges of kaolinite which can bond Cd by stronger forces than just coulombic attraction. Cadmium bound by organic matter also increased slightly with time which could be attributed to the development of some additional specific adsorption sites within the organic matter particles rather than at the surfaces. The transformation of exchangeable Cd to other forms (residual and bound to organic matter) was affected by the rate of Cd addition which also reflects the formation of a limited number of specific adsorption sites. At pH 6, the transformation of exchangeable Cd to residual Cd continued up to the fourth day of incubation whereas, at pH 7, the transformation continued for a longer period of time, especially at the lower rate of Cd addition. A possible explanation for this may be that the strength of binding by exchangeable and residual sites becomes more similar at higher pH and hence there is less transformation of the exchangeable forms to the residual forms.

Time had no effect on any of the forms of Cd in the peaty sand at pH <5, presumably because Cd reacts with exchange sites (the major form) very rapidly. At pH values $\geq$5, soluble Cd and Cd bound to organic matter increased with time, whereas exchangeable Cd decreased, suggesting that organic matter became the main adsorption component of the soil due to the development of pH-dependent adsorption sites. The effect of time on the forms of Cd in the peaty sand was affected the least by the Cd application rate, indicating that there were enough sites on the organic matter to adsorb most of the Cd applied at pH $\geq$5. The reactions tended to be faster initially and then slowed down with time. Aringhieri *et al.* (1985) observed that 80% of adsorption took place within 10 min of Cd addition to a soil containing high organic matter (14·2%) and high clay content (60%). A slight increase in the soluble form of Cd at pH 7 was also observed with time which is possibly due to the slow dissolution of organic matter at higher pH values, subsequently releasing Cd into the soil solution (Borggaard 1979).

In the siliceous sand, the soluble form of Cd decreased with time, whereas the exchangeable form of Cd increased. Most of the Cd applied to the siliceous sand

stayed in soluble and/or exchangeable forms (>95%) at all the pH values because of the soil's limited adsorption capacity due to the absence of adsorption components (i.e. organic matter, oxides and clays). At pH 4, no change in these forms with time was observed at the highest rate of Cd application because of a limited number of exchange sites (Figs 8*a* and 8*c*). At application rates $\leq 3 \cdot 2\ \mu g\ g^{-1}$, the decrease in soluble Cd and the concomitant increase in exchangeable Cd at all pH values suggested that there were sufficient exchange sites for the amount of Cd applied. At the highest rate, a decrease in soluble Cd with time was noticed at pH > 5, presumably because sufficient sites were only available above this pH. However, the extent of the decrease did not increase as pH rose from 5 to 7 (i.e. the number of sites increased), possibly because the rate of exchange is pH dependent and increased with pH due to less competition with cations such as H^+.

In soils where Cd was not added but was already present as native Cd (the yellow earth and lateritic podzolic soils), most of it was extracted as residual Cd (i.e. $0 \cdot 07$ and $0 \cdot 14\ \mu g\ g^{-1}$ respectively) and no change in any of the forms of Cd with time was observed. This suggested that native Cd was derived from the parent material where it was either entrapped/occluded in the phyllosilicate and sesquioxide minerals (Rudd *et al.* 1984). Alternatively, the yellow earth and lateritic podzolic soils were contaminated with Cd from a source which slowly diffused into less accessible sites with time (Brummer *et al.* 1988; Barrow *et al.* 1989).

The amounts of soluble and exchangeable Cd are indications of the most labile or bioavailable forms in the soil (LeClaire *et al.* 1984) and, hence, their transformation to other forms with time suggested a decrease in availability of Cd. This is in agreement with the findings of Street *et al.* (1978) who found that increasing the incubation time decreased the availability of Cd to plants. However, in soils such as the siliceous sand (irrespective of time since Cd application), the transformation of soluble Cd will be restricted to exchangeable and precipitated forms only.

Conclusions

An increase in the time of contact of Cd decreased the soluble and the exchangeable forms of Cd in all the soils except the siliceous sand. These changes have the potential to decrease the risk of Cd loss to groundwater by leaching and the risk of Cd uptake by plants. However, the rate and extent of the decrease in soluble and exchangeable forms of Cd with time (and hence, the risk) depended upon the type and relative proportion of the adsorption surfaces present in the soil, pH and the rate of Cd addition.

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